


PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference R3214-PCT	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/BE2005/000030	International filing date (day/month/year) 25.02.2005	Priority date (day/month/year) 26.02.2004
International Patent Classification (IPC) or national classification and IPC C07C6/00, C07F19/00, C07F15/00		
Applicant UNIVERSITEIT GENT et al.		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 18 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand 23.12.2005	Date of completion of this report 07.02.2006	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Elliott, A Telephone No. +49 89 2399-8218	



**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/BE2005/000030

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-6, 8-89	as originally filed
7, 7bis	received on 29.12.2005 with letter of 23.12.2005

Claims, Numbers

1-57	received on 29.12.2005 with letter of 23.12.2005
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Drawings, Sheets

1/10-10/10	as originally filed
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☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-57
	No: Claims	-
Inventive step (IS)	Yes: Claims	1-57
	No: Claims	-
Industrial applicability (IA)	Yes: Claims	1-57
	No: Claims	-

2. Citations and explanations (Rule 70.7):

see separate sheet

The following documents are referred to in this report:

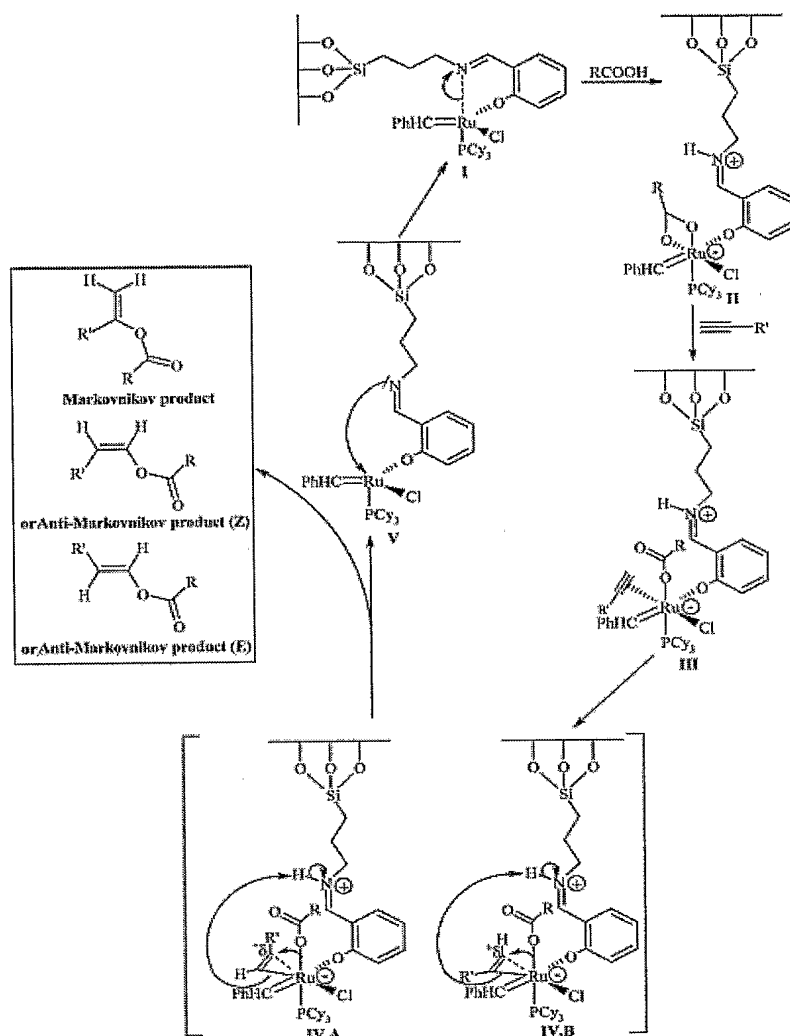
- D1: WO 99/22865 A (CALIFORNIA INSTITUTE OF TECHNOLOGY) 14 May 1999
D2: CLERCQ B D ET AL: "Immobilization of multifunctional Schiff base containing ruthenium complexes on MCM-41"
APPLIED CATALYSIS A: GENERAL, vol. 247, no. 2, 25 July 2003, pages 345-364

Re Item V

Novelty / Inventive Step

The application discusses D1 in what would appear quite some detail in the present description and the conclusion reached would appear to be that what is now being claimed is somehow different to D1's disclosure. D1 is directed to the "acid activation of ruthenium metathesis catalysts" which would appear to be what the present application is directed to as well. Referring to Example 7 of D1 (pages 28 & 29), the deuterium marker is seen to deuterate the phosphine ligand. However, the ruthenium complex being subjected to reaction with DCl is not a ruthenium complex having coordinated thereto a Schiff base. Catalyst 4 of D1 is one in which a Schiff base is coordinated to the central ruthenium atom. The reaction of this species with DCl was not scrutinised in D1.

Moving on to D2 (written by one of the present inventors), let us look at Scheme 3 on page 361:



In association with this scheme, it is stated that "the first step involves a "one-arm" dissociation of the bidentate Schiff base ligand" (page 260, column 2). Species I in Scheme 3 is a ruthenium complex having both a Schiff base ligand and a phosphine ligand but it is the Schiff base that is protonated by the carboxylic acid and not the phosphine. Therefore the mechanism on which the present application relies is known from D2.

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

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Claim 1 of the present application in its original format stated in its last 2 lines that "other ligands (ii) are selected such as to be unable of protonation by said acid under said conditions". In amended form, this now reads: "other ligands (ii) are selected such as to be unable of protonation by said acid under said conditions, and are not selected from the group consisting of phosphines, amines, arsines and stilbines." In D2 it does not appear that the phosphine ligand is protonated but with the claims having been amended to exclude the possibility that the "other ligands" do not include phosphines, the claims of the present application are to be regarded as novel over D1 and D2 in amended format.

As regards inventive step, with D1 and D2 only actually employing ruthenium catalysts containing phosphine ligands, the question which needs to be asked is whether it would be obvious for the skilled person to assume that the mechanism of D2 is valid for other ruthenium catalysts having a ligand other than a phosphine, an arsine, a stilbine or an amine. With the commonly known coordinating ligands having been excluded, it seems very unlikely that the skilled person would envisage broadening the teaching of D1 or D2 or their combination to other catalysts. It would therefore appear possible to acknowledge an inventive step on these grounds.

resonance) and that the effect of the acid in the system appears to be twofold: in addition to eliminating hydroxide ions which would cause catalyst decomposition, catalyst activity is also enhanced by protonation of phosphine ligands. It is also taught that, remarkably, the acids do not react with the ruthenium alkylidene bond.

5 Although providing an improvement over existing ROMP catalysts, the teaching of U.S. Patent No. 6,284,852 is limited in many aspects, namely:

- because its alleged mechanism of acid activation involves the protonation of phosphine ligands, it is limited to alkylidene ruthenium complexes including at least one phosphine ligand;
- 10 - it does not disclose reacting a Schiff-base-substituted ruthenium complex with an acid under conditions such that said acid at least partly cleaves a bond between the metal and the Schiff base ligand of said ruthenium complex.

U.S. Patent No. 6,284,852 does not either teach the behaviour, in the presence of an acid, of ruthenium complexes wherein ruthenium is coordinated with a vinylidene
15 ligand, an allenylidene ligand or a N-heterocyclic carbene ligand.

U.S. Patent No. 6,284,852 therefore has left open ways for the study of metal complexes, in particular multicoordinated ruthenium and osmium complexes in an acidic, preferably a strongly acidic, environment when used for olefin metathesis reactions including ROMP, RCM, ADMET and cross-metathesis and dimerization
20 reactions.

Applied catalysis A (2003) 247:345 discloses the catalytic behavior of Schiff base and phosphine containing ruthenium complexes having been covalently anchored to a solid support. In this document, vinylation experiments are described where a large amount of a carboxylic acid (110 eq/cat) is used as a reactant. This document further
25 postulates a mechanism that explains for observed selectivities in vinylation experiments. In that mechanism, a first step involves a "one arm" dissociation of the bidentate Schiff base ligand, followed by coordination of an allylic carboxylate group. *Applied catalysis A* (2003) 247:345 does not report improvement of the catalytic activity that would be induced by the presence of the acid.

30 Therefore one goal of this invention is the design of new and useful catalytic species, especially based on multicoordinated transition metal complexes, having unexpected properties and improved efficiency in olefin metathesis reactions as well as in other atom or group transfer reactions such as ATRP or ATRA.

Another goal of this invention is to efficiently perform olefin metathesis reactions, in
35 particular ring opening polymerization of strained cyclic olefins (including cationic forms of such monomers such as, but not limited to, strained cyclic olefins including

quaternary ammonium salts), in the presence of multicoordinated transition metal complexes without being limited by the requirement of a phosphine ligand in said complexes.

- There is also a specific need in the art, which is yet another goal of this
- 5 invention, for improving reaction-injection molding (RIM) processes, resin transfer molding (RTM) processes and reactive rotational molding (RRM) processes such as, but not limited to, the bulk polymerisation of endo- or exo-dicyclopentadiene, or copolymerization thereof with other monomers, or formulations thereof, with the use of multicoordinated transition metal complexes, in particular ruthenium complexes, having
- 10 various combinations of ligands but which do not necessarily comprise phosphine ligands. All the above needs

1. A method of modifying a multi-coordinated metal, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further
5 heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, said method comprising bringing said multi-coordinated metal complex into contact with an acid under conditions such that said acid is able to at least partly cleave a bond between the metal and said at least one multidentate Schiff base ligand (i), and wherein said other ligands (ii) are selected such as to be
10 unable of protonation by said acid under said conditions, and are not selected from the group consisting of phosphines, amines, arsines and stibines
2. A method according to claim 1, characterized in that said conditions include a molar ratio between said acid and said multi-coordinated metal complex being above 1.2 and
15 below 40.
3. A method according to claim 1 or claim 2, characterized in that said conditions include a contact time from 5 seconds to 100 hours.
- 20 4. A method according to any of claims 1 to 3, characterized in that said conditions include a contact temperature from about -50°C to about $+80^{\circ}\text{C}$.
5. A method according to any of claims 1 to 4, wherein the pK_a of said acid is lower than the pK_a of said multidentate Schiff base ligand (ii).
25
6. A method according to any of claims 1 to 5, characterized in that at least one of said other ligands (ii) is a constraint steric hindrance ligand having a pK_a of at least 15.
7. A method according to any of claims 1 to 6, characterized in that the number of
30 carbon atoms in said at least one multidentate Schiff base ligand (i), between the nitrogen atom of said imino group and said coordinating heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.
8. A method according to any of claims 1 to 7, characterized in that at least one of said
35 other ligands (ii) is a carbene ligand selected from the group consisting of N-

heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.

5 9. A method according to any of claims 1 to 7, characterized in that at least one of said other ligands (ii) is an anionic ligand.

10. A method according to any of claims 1 to 7, characterized in that at least one of said other ligands (ii) is a non-anionic ligand.

10 11. A method according to any of claims 1 to 10, characterized in that said acid is chlorhydric acid or bromhydric acid.

15 12. A method according to any of claims 1 to 11, characterized in that said conditions are able to protonate the multidentate Schiff base ligand and decoordinate the nitrogen atom of the imino group of said multidentate Schiff base ligand from the metal.

20 13. A method according to any of claims 1 to 12, characterized in that said conditions are able to decoordinate the further heteroatom of said multidentate Schiff base ligand from the metal.

14. The reaction product of:

25 (a) a multi-coordinated metal complex, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, and

(b) an acid reacted in a molar ratio above about 1.2 with respect to said multi-coordinated metal complex (a),

30 provided that said other ligands (ii) are unable of protonation by said acid and are not selected from the group consisting of amines, phosphines, arsines and stibines

35 15. A product according to claim 14, characterized in that the pKa of said acid (b) is lower than the pKa of said at least one multidentate Schiff base ligand (i).

16. A product according to any of claims 14 to 15, characterized in that the number of carbon atoms in said at least one multidentate Schiff base ligand (i), between the nitrogen atom of said imino group and said heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.

17. A product according to any of claims 14 to 16, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a constraint steric hindrance ligand having a pKa of at least 15.

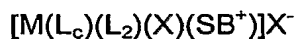
18. A product according to any of claims 14 to 17, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand selected from the group consisting of N-heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.

19. A product according to any of claims 14 to 17, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand.

20. A product according to any of claims 14 to 17, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand.

21. A product according to any of claims 14 to 20, characterized in that said acid is chlorhydric acid or bromhydric acid.

22. A product according to any of claims 14 to 21, being a monometallic species represented by the general formula:



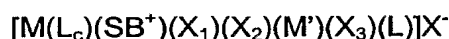
wherein

- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- SB^+ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff base ligand;

- L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
- L_2 is a non-anionic ligand;
- X is an anionic ligand; and
- X^- is an anion,

salts, solvates and enantiomers thereof.

23. A product according to any of claims 14 to 21, being a bimetallic species represented by the general formula:

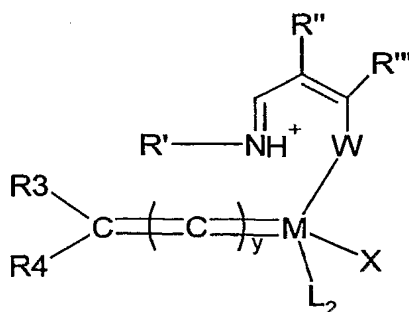


wherein

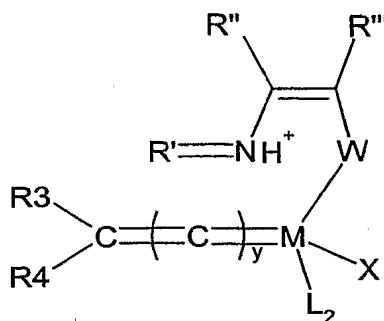
- M and M' are each a metal independently selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- SB^+ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff base ligand;
- L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
- L is a non-anionic ligand;
- X_1 , X_2 and X_3 are each independently selected from anionic ligands; and
- X^- is an anion,

salts, solvates and enantiomers thereof.

24. A product according to any of claims 14 to 21, being a cationic monometallic species being represented by the general formula (VI):



or a cationic monometallic species being represented by the general formula (VII):

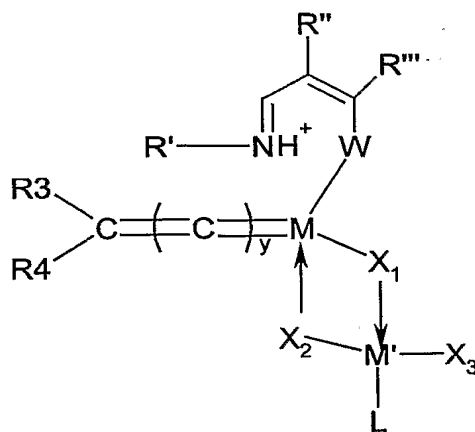


wherein

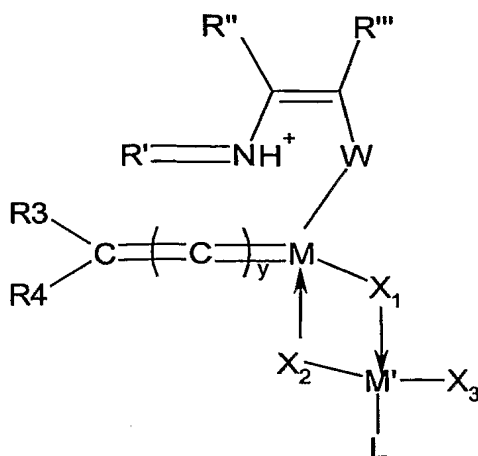
- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR''' , PR''' , AsR''' and SbR''' ;
- R'' , R''' and R''' are each a radical independently selected from the group consisting of hydrogen, C_{1-6} alkyl, C_{3-8} cycloalkyl, C_{1-6} alkyl- C_{1-6} alkoxy, C_{1-6} alkyl-aryloxy, C_{1-6} alkyl- C_{3-10} cycloalkoxy, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R_5 each independently selected from the group consisting of halogen atoms, C_{1-6} alkyl, C_{1-6} alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C_{1-6} alkyl- C_{1-6} alkoxy, C_{1-6} alkyl-aryloxy, C_{1-6} alkyl- C_{3-10} cycloalkoxy, alkylammonium and arylammonium;
- R' is either as defined for R'' , R''' and R''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C_{1-6} alkylene and C_{3-8} cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R_5 ;
- L_2 is a non-anionic ligand;
- X is an anionic ligand;

- R_3 and R_4 are each hydrogen or a radical selected from the group consisting of C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} carboxylate, C_{1-20} alkoxy, C_{2-20} alkenyloxy, C_{2-20} alkynyloxy, aryl, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-8} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl, C_{1-20} alkylsulfonate, arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium and arylammonium;
 - R' and one of R_3 and R_4 may be bonded to each other to form a bidentate ligand;
 - R'' and R''' may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;
 - R_3 and R_4 together may form a fused aromatic ring system, and
 - y represents the number of sp_2 carbon atoms between M and the carbon atom bearing R_3 and R_4 and is an integer from 0 to 3 inclusive,
- salts, solvates and enantiomers thereof, and said cationic species being associated with an anion.

25. A product according to any of claims 14 to 21, being a cationic bimetallic species being represented by the general formula (X):



or a cationic bimetallic species being represented by the general formula (XI):



wherein

- M and M' are each a metal independently selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR''', PR''', AsR''' and SbR''';
- R'', R''' and R'''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, alkylammonium and arylammonium;
- R' is either as defined for R'', R''' and R'''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₆ alkylene and C₃₋₈ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅;

- $$\begin{array}{c} \text{R3} \\ \diagdown \\ \text{C} = (\text{C})_y \text{M} \begin{array}{l} \diagup \text{X} \\ \text{---} \text{X}' \\ \diagdown \text{L}_3 \end{array} \\ \diagup \\ \text{R4} \end{array}$$

28. A product according to claim 27, characterized in that one metal of said bimetallic complex is penta-coordinated with said at least one multidentate Schiff base ligand (i)

and with said one or more other ligands (ii), and the other metal is tetra-coordinated with one or more neutral ligands and one or more anionic ligands.

5 29. A product according to claim 27, characterized in that each metal of said bimetallic complex is hexa-coordinated with said at least one multidentate Schiff base ligand (i) and with said one or more other ligands (ii).

10 30. A product according to claim 27, characterized in that the two metals of the bimetallic complex are the same.

31. A product according to claim 27, characterized in that the two metals of the bimetallic complex are different.

15 32. A product according to any of claims 14 to 21, characterized in that said multi-coordinated metal complex (a) is a monometallic complex.

20 33. A product according to any of claims 14 to 21, characterized in that the metal of said multi-coordinated metal complex (a) is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table.

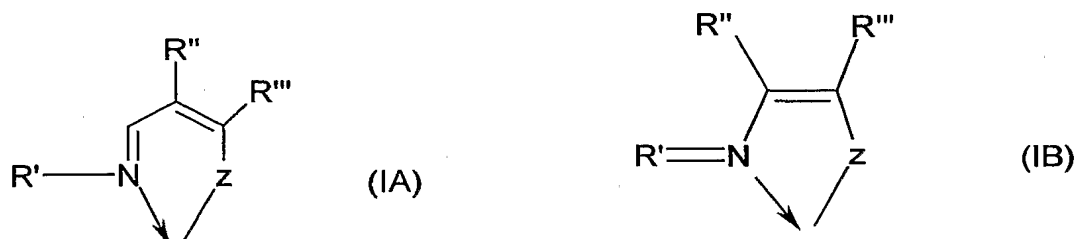
25 34. A product according to any of claims 14 to 21, characterized in that said metal is selected from the group consisting of ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

35. A product according to any of claims 14 to 21, characterized in that said multi-coordinated metal complex (a) is a penta-coordinated metal complex or a tetra-coordinated metal complex.

30 36. A product according to claim 35, characterized in that said at least one multidentate Schiff base ligand (i) is a bidentate ligand and said multi-coordinated metal complex (a) comprises two other ligands (ii).

37. A product according to claim 35, characterized in that said at least one multidentate Schiff base ligand (i) is a tridentate ligand and said multi-coordinated metal complex (a) comprises a single other ligand (iii).

- 5 38. A product according to claim 35 or claim 36, characterized in that said at least one multidentate Schiff base ligand (i) has one of the general formulae (IA) and (IB):



wherein:

- Z is selected from the group consisting of oxygen, sulfur and selenium;
 - 10 - R'' and R''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, 15 C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, alkylammonium and arylammonium;
 - 20 R' is either as defined for R'' and R''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₇ alkylene and C₃₋₁₀ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅.
- 25 39. A product according to claim 35, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a derivative, wherein one or more hydrogen atoms is substituted with a group providing constraint steric hindrance, of a N-heterocyclic carbene selected from the group consisting of imidazol-2-ylidene, dihydroimidazol-2-ylidene, oxazol-2-ylidene, triazol-5-ylidene, thiazol-2-ylidene, 30 bis(imidazol-2-ylidene), bis(imidazolidin-2-ylidene), pyrrolylidene, pyrazolylidene,

dihydro-pyrrolylidene, pyrrolylidinylidene and benzo-fused derivatives thereof, or a non-ionic prophosphatane superbase.

40. A product according to claim 35, characterized in that at least one of said other
5 ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand selected from the group consisting of C₁₋₂₀ alkyl, C₁₋₂₀ alkenyl, C₁₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₁₋₂₀ alkenyloxy, C₁₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium, arylammonium, halogen
10 atoms and cyano.

41. A product according to claim 35, characterized in that at least one of said other
ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand represented
by the general formula $=[C=]_yCR_3R_4$, wherein:

- 15
- y is an integer from 0 to 3 inclusive, and
 - R₃ and R₄ are each hydrogen or a hydrocarbon radical selected from the group consisting of C₁₋₂₀ alkyl, C₁₋₂₀ alkenyl, C₁₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₁₋₂₀ alkenyloxy, C₁₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate,
20 C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium; or R₃ and R₄ together may form a fused aromatic ring system.

42. A product according to claim 41, characterized in that R₃ and R₄ together form a
fused aromatic ring system such that said other ligand (ii) of said multi-coordinated
25 metal complex (a) is a phenylindenylidene ligand.

43. A product according to claim 35, characterized in that at least one of said other
ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic unsaturated
ligand L¹ selected from the group consisting of aromatic and unsaturated cycloaliphatic
30 groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

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44. A product according to claim 35, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand L^2 selected from the group consisting of C_{1-7} alkyl, C_{3-10} cycloalkyl, arylalkyl and heterocyclic, the said group being optionally substituted with one or more preferably
5 electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

45. A product according to claim 35, characterized in that said at least one multidentate
10 Schiff base ligand (i) is a tetradentate ligand and said multi-coordinated metal complex (a) comprises one or two other ligands (ii) being non-anionic ligands L^7 selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C_{4-20} cycloalkenyl groups, wherein the said aromatic or unsaturated cycloaliphatic group is optionally substituted with one or more C_{1-7} alkyl groups or
15 electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

46. A product according to claim 14, wherein said acid (b) is an acid generated *in situ*
20 from a photoacid generator.

47. A product according to claim 14, comprising the product of at least partial cleavage
of a bond between the metal and said at least one multidentate Schiff base ligand
(i).
25

48. A catalytic system comprising:

(a) as the main catalytic species, a reaction product according to any of
claims 14 to 47, and

(b) one or more second catalyst components being selected from the group
30 consisting of Lewis acid co-catalysts (b_1), catalyst activators (b_2), and
initiators having a radically transferable atom or group (b_3).

49. A catalytic system according to claim 48, wherein the second catalyst component
includes a co-catalyst (b_1) selected from the group consisting of boron trihalides;
35 phosphorus trihalides; trialkylboron compounds; triarylboron compounds;

organoaluminum compounds; magnesium dihalides; aluminum trihalides; tin tetrachloride; titanium or vanadium trihalides or tetrahalides or tetraalkoxides; antimony and bismuth pentahalides.

5 50. A catalytic system according to claim 48, wherein the second catalyst component includes, as a catalyst activator (b_2), a diazo compound.

10 51. A catalytic system according to claim 48, wherein the second catalyst component includes, as an initiator having a radically transferable atom or group (b_3), a compound having the formula $R_{35}R_{36}R_{37}CX_1$, wherein:

- 15 - X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C_{1-7} alkyl groups and phenyl-substituted C_{1-7} alkyl), SR_{39} , $OC(=O)R_{39}$,
20 $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O--N(R_{39})_2$ and $S--C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present, the two R_{39} groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of heteroaryl above), and
- 25 - R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-6} alkyl), C_{3-8} cycloalkyl, $C(=O)R_{40}$, (wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form an alkylene group of 2 to 5 carbon atoms), $COCl$, OH , CN , C_{2-20} alkenyl (preferably vinyl), C_{2-20} alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C_{2-20} alkenyl.

52. A supported catalyst, comprising:

- 30 (a) a catalytically active reaction product according to any of claims 14 to 47, or a catalytic system according to claim 48, and
- (b) a supporting amount of a carrier suitable for supporting said catalytically active product or catalytic system (a).

35 53. A method of performing an olefin or acetylene metathesis reaction or a reaction involving the transfer of an atom or group to an ethylenically or acetylenically

unsaturated compound or another reactive substrate in the presence of a catalytic component, wherein the said catalytic component comprises a product according to any of claims 14 to 47 or a catalytic system according to any of claims 48 to 51.

- 5 54. A method according to claim 53, wherein said reaction involving the transfer of an atom or group to an olefin or another reactive substrate is selected from the group consisting of:
- 10 - atom or group transfer radical polymerisation of one or more radically (co)polymerisable monomers, especially mono- and diethylenically unsaturated monomers;
 - atom transfer radical addition of a polyhalomethane having the formula CX_nH_{4-n} , wherein X is halogen and n is an integer from 2 to 4, onto an ethylenically unsaturated compound to produce the corresponding saturated polyhalogenated adduct;
 - 15 - vinylation reaction of a mono- or di-alkyne with a mono- or di-carboxylic acid to produce alk-1-enyl esters or enol esters or Markovnikov adducts or anti-Markovnikov adducts or mixtures thereof;
 - cyclopropanation of an α -ethylenically unsaturated compound for producing an organic compound having one or more cyclopropane structural units;
 - 20 - quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones;
 - epoxidation of α -ethylenically unsaturated compounds for producing epoxides;
 - oxidation of organic compounds including the oxidation of saturated hydrocarbons for producing alcohols, or sulfides for producing sulfoxides and sulfones, or phosphines for producing phosphonates, or alcohols and aldehydes for producing carboxylic acids;
 - 25 - cyclopropenation of an alkyne for producing an organic compound having one or more cyclopropene structural units;
 - hydrocyanation of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for producing β -cyano carbonyl compounds;
 - 30 - hydrosilylation of olefins for producing saturated silanes, or alkynes for producing unsaturated silanes, or ketones for producing silyl ethers, or trimethylsilylcyanation of aldehydes for producing cyanohydrin trimethylsilyl ethers;
 - 35

- aziridination of imines or alkenes for producing organic compounds having one or more aziridine structural units;
- hydroamidation of olefins for producing saturated amides;
- hydrogenation of olefins for producing alkanes, or ketones for producing alcohols;
- aminolysis of olefins for producing saturated primary or secondary amines;
- isomerisation of alcohols, preferably allylic alcohols, for producing aldehydes;
- Grignard cross-coupling of alkyl or aryl halides for producing alkanes or arylalkanes;
- hydroboration of olefins for producing alkylboranes and trialkylboranes;
- hydride reduction of aldehydes and ketones for producing alcohols;
- aldol condensation of saturated carboxyl compounds for producing α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intramolecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds;
- Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds;
- Robinson annulation for producing saturated polycyclic carboxyl compounds;
- Heck reactions of an aryl halide or a 1-hetero-2,4-cyclopentadiene or a benzo-fused derivative thereof with an α -ethylenically unsaturated compound for producing arylalkenes or heteroarylalkenes;
- codimerisation of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes;
- hydroxylation of olefins for producing alcohols;
- hydroamination of olefins and alkynes for producing amines;
- alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones; and
- Diels-Alder reactions such as the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated compound for producing optionally substituted 7-oxanorbornenes.

55. A method according to claim 53, wherein the said metathesis reaction is the ring-opening metathesis polymerisation of strained cyclic olefins.

56. A method according to claim 53, wherein the catalytic component is supported on a carrier.
- 5 57. A method according to claim 56, wherein the said carrier is selected from the group consisting of porous inorganic solids, such as amorphous or paracrystalline materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins.